Karlsruhe Institute of Technology

Institute for Applied Materials

High-temperature oxidation and mutual interactions of materials during severe nuclear accidents

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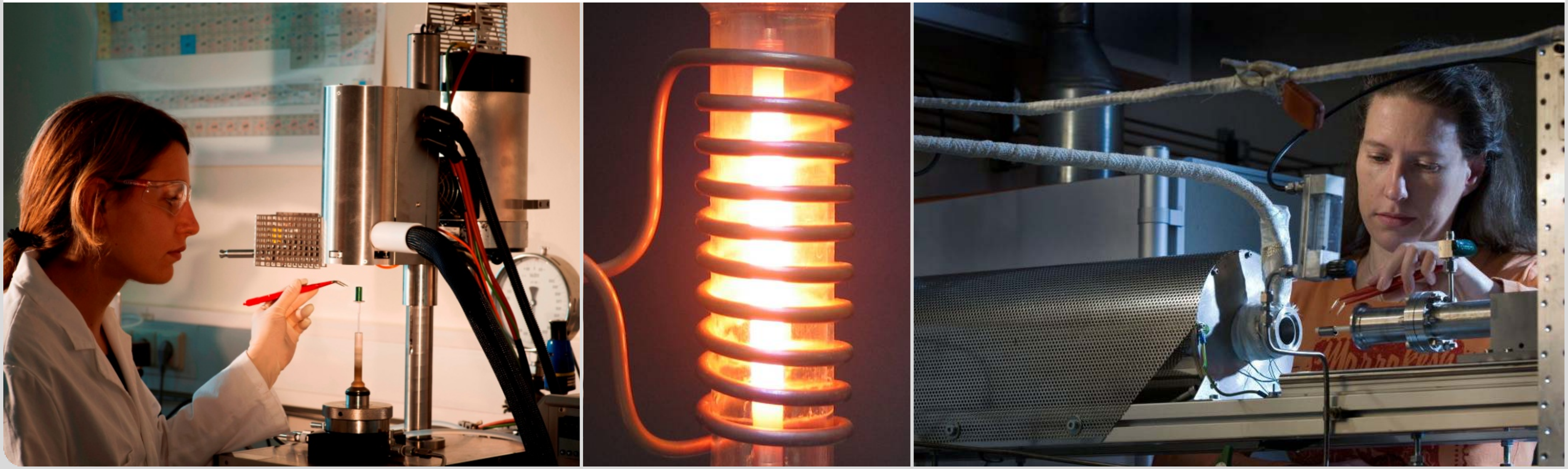


Karlsruhe Institute of Technology

Founded in 2009

= FZK research center (1956) + University Karlsruhe (1825)

= 9000 employees

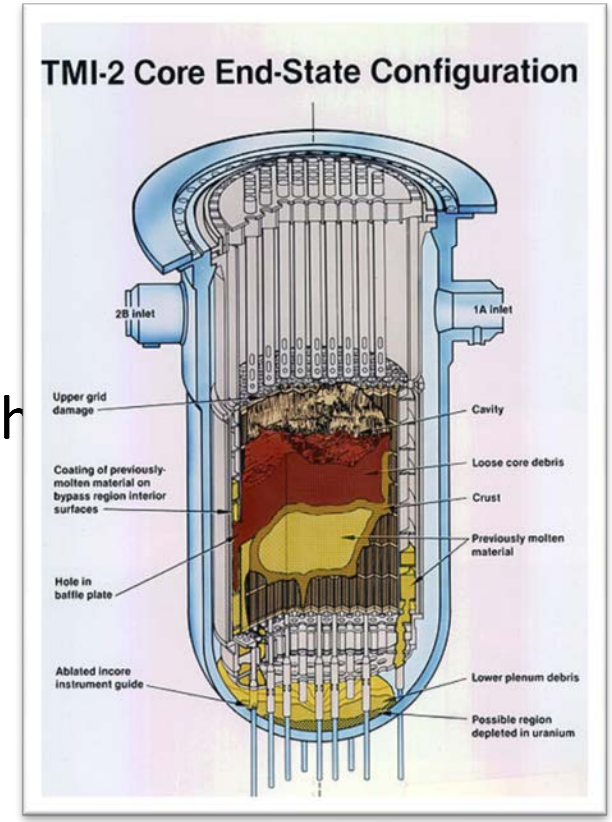
= 23 000 students

Outline

- Phenomenology of severe accidents in light water reactors (LWR)
- High-temperature oxidation of zirconium alloys in various atmospheres
- Behavior of boron oxide control rods during severe accidents
- Silver-indium-cadmium control rod failure during severe accidents

LWR severe accident scenario

- Loss of coolant causes steady heatup of the core due to residual decay heat
- From ca. 1000°C oxidation of zirconium alloy cladding becomes significant
- From ca. 1250°C chemical interactions between the different core materials (stainless steel, Zr alloys, boron carbide …) lead to the local formation of melts significantly below the melting temperatures of the materials
- From ca. 1800°C formation of melt pool in th core and relocation of melt/debris to the lower plenum (in-vessel, see TMI-2).
- Subsequently, failure of the RPV and release of corium melt into the containment (ex-vessel, see Fukushima)


TMI-2 Core End-State Configuration

Core materials in Light Water Reactors

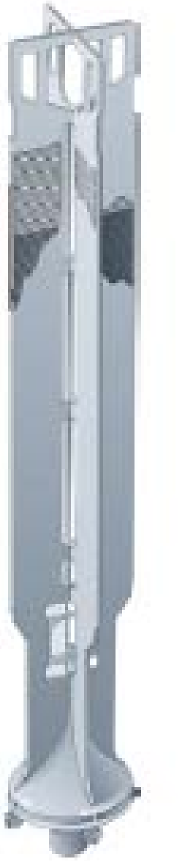
UO_2(/PuO_2) fuel:	100-200 t
Zry cladding + grid spacers:	20-40 t
Zry canister (BWR):	40 t
Various steels, Inconel:	>500 t (incl. RPV)
B_4C absorber (BWR, VVER, …):	0.3-2 t
AgInCd absorber (PWR):	3-5 t

Environment

- **Water, steam**
- Air
- Nitrogen

} After failure of RPV/primary circuit

PWR fuel assembly



BWR control blade

High-temperature oxidation of zirconium alloys

- Most cladding alloys consist of 98-99 wt% zirconium plus some alloying elements (Sn, Nb, Fe, Cr, …)

Element	Zircaloy-4	D4	M5	E110	ZIRLO
Nb	-	-	**1**	**1**	**1**
Sn	**1.5**	**0.5**	0.01	**-**	**1**
Fe	0.2	**0.5**	0.05	0.008	0.11
Cr	0.1	0.2	0.015	0.002	< 0.01

- In steam, oxygen, nitrogen, air, and various mixtures
- Temperature: 600-1600°C

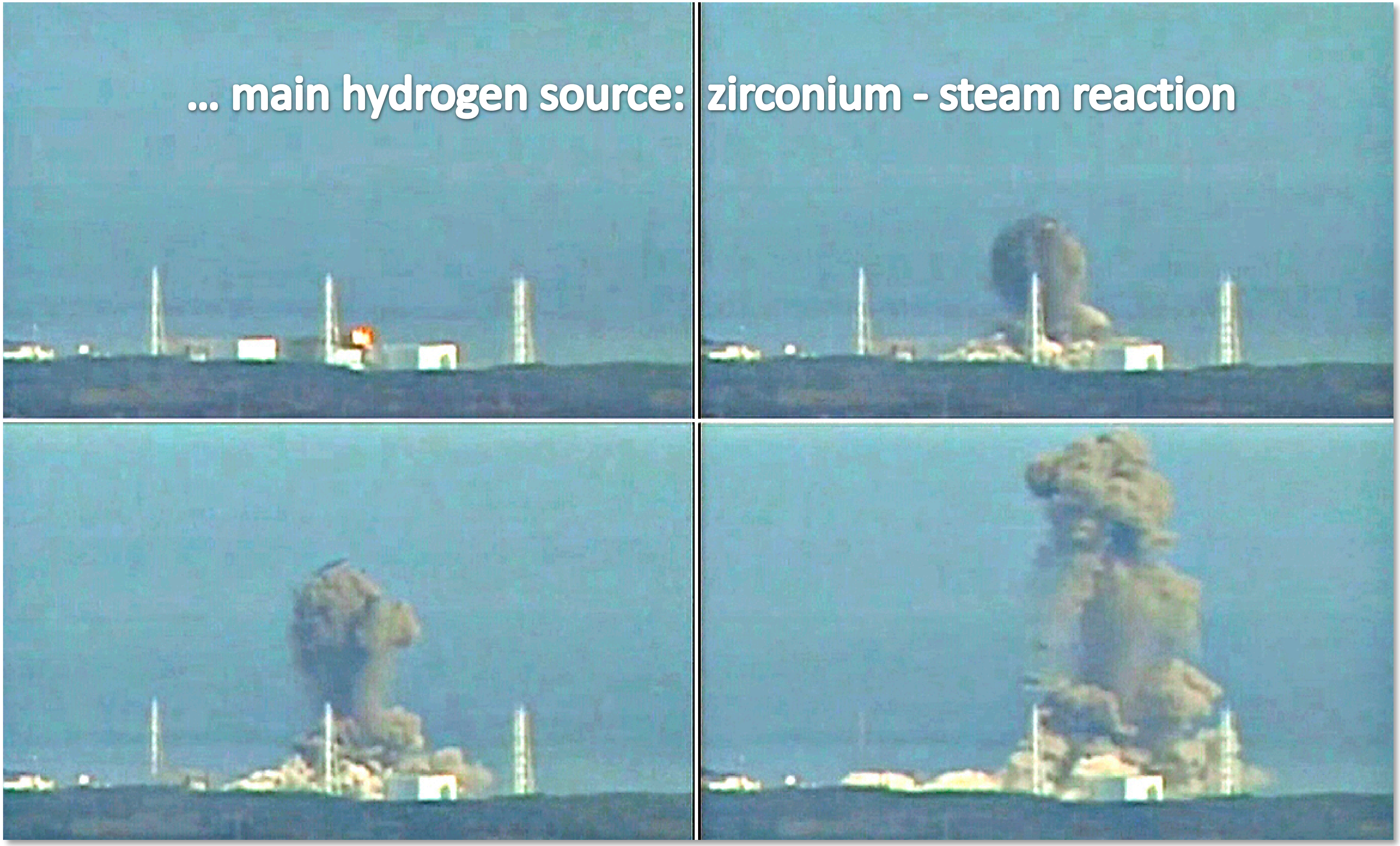
Oxidation of zirconium alloys – chemical reactions

ΔH_f at 1500 K

$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$	-585 kJ/mol
$Zr + O_2 \rightarrow ZrO_2$	-1083 kJ/mol
$Zr + 0.5N_2 \rightarrow ZrN$	-361 kJ/mol

- Release of hydrogen and heat
- Hydrogen either released to the environment or absorbed by Zr metal

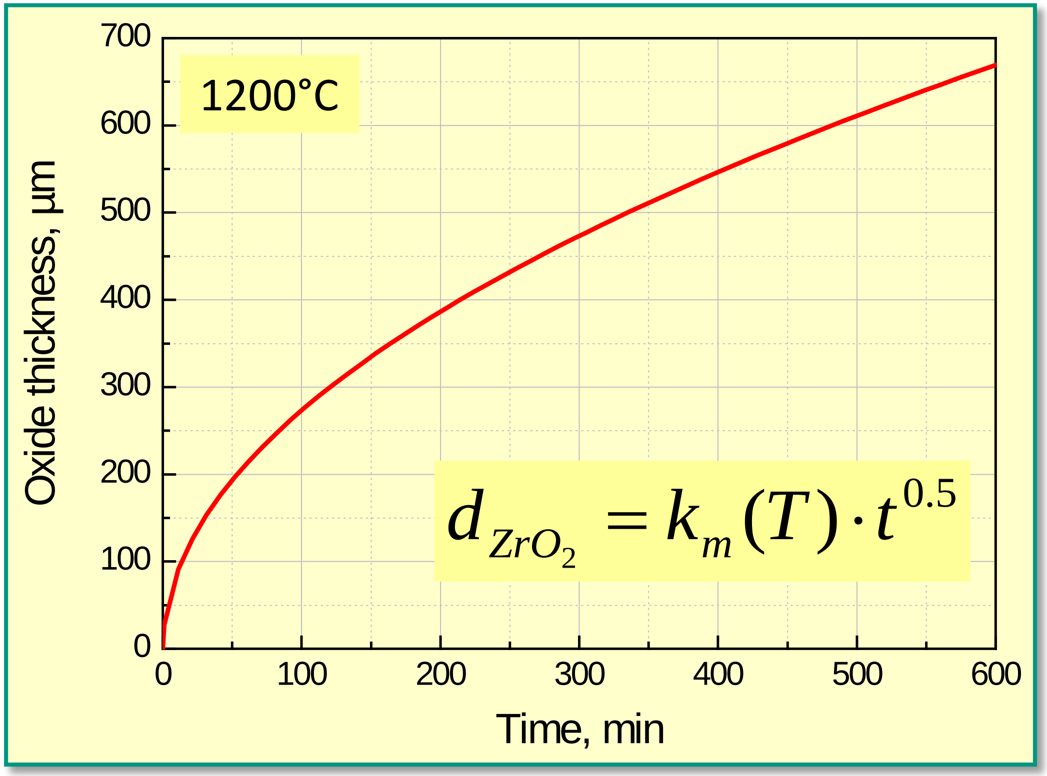
Hydrogen detonation in Fukushima Dai-ichi NPPs …



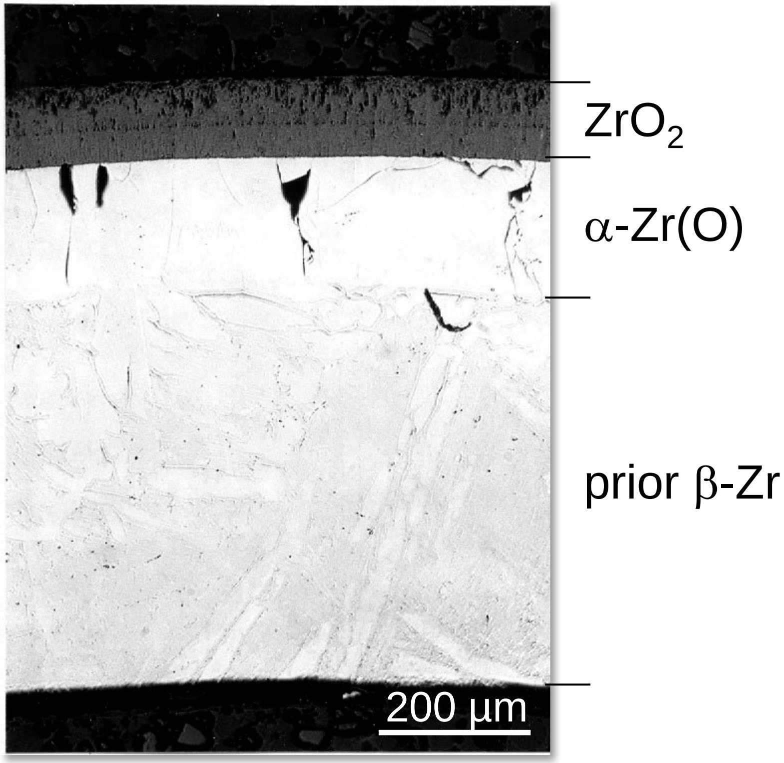
… main hydrogen source: zirconium - steam reaction

Oxidation in steam (oxygen)

- Most LOCA and SFD codes use parabolic oxidation correlations (determined by the diffusion of oxygen through growing oxide scale)



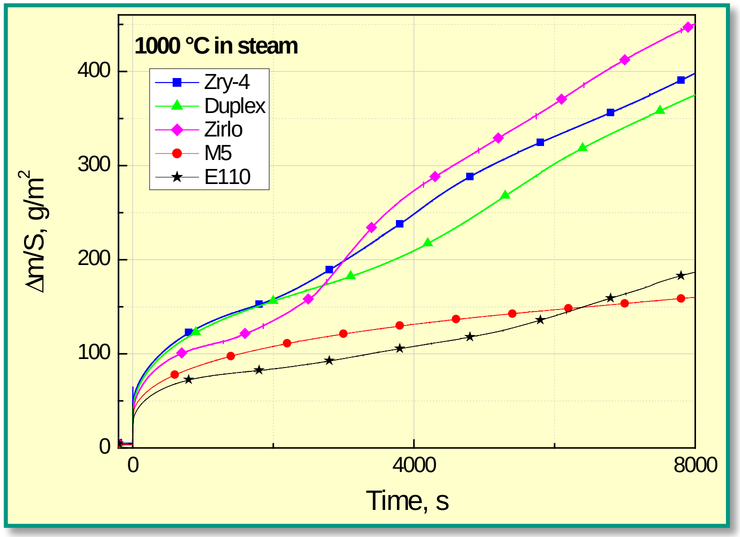
Oxide thickness during oxidation of Zry at 1200°C in steam

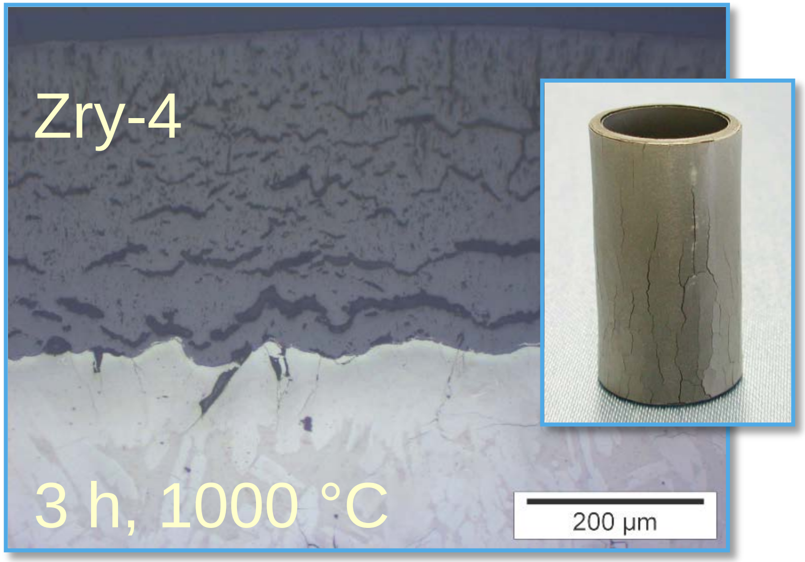


20 min at 1200°C in steam

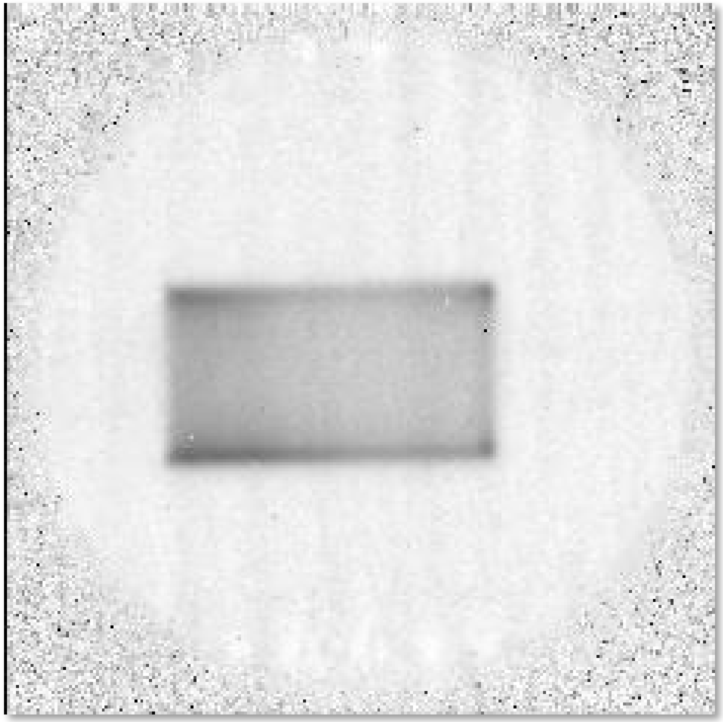
Breakaway oxidation

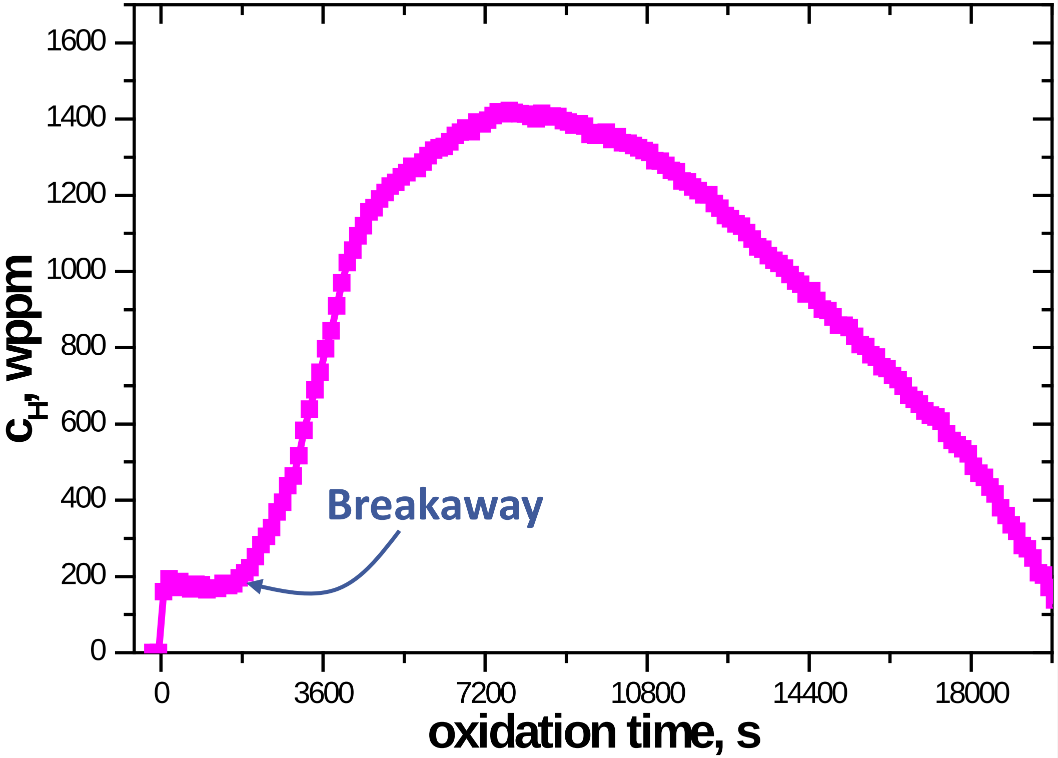
- Loss of protective properties of oxide scale due to its mechanical failure.
- Breakaway is caused by phase transformation from pseudo-stable tetragonal to monoclinic oxide and corresponding change in density up to ca. 1050°C.
- Critical times and oxide thicknesses for breakaway strongly depend on type of alloy and boundary conditions (ca. 30 min at 1000°C and 8 h at 600°C).
- During breakaway significant amounts of hydrogen can be absorbed (>40 at.%, 7000 wppm) due to local enrichment of H_2 in pores and cracks near the metal/oxide boundary ("hydrogen pump").





In-situ investigation of hydrogen uptake during oxidation of Zry in steam by neutron radiography





Zry-4, 1000°C
30 g/h steam, 30 l/h argon

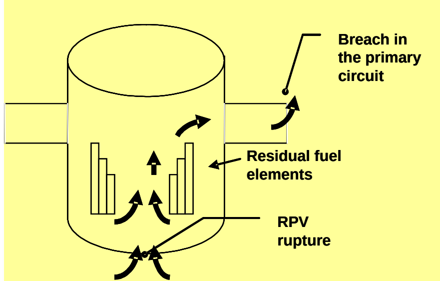
- Rapid initial hydrogen uptake
- Further strong hydrogen absorption after transition to breakaway

Oxidation in atmospheres containing nitrogen

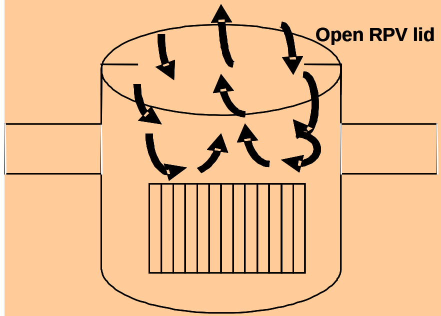
- Air ingress into reactor core, spent fuel pond, or transportation cask
- Nitrogen in BWR containments (inertization) and ECCS pressurizers
- Prototypically following steam oxidation and mixed with steam

- Consequences:
  - Significant heat release causing temperature runaway from lower temperatures than in steam
  - Strong degradation of cladding causing early loss of barrier effect
  - High oxygen activity influencing FP chemistry and transport

Late phase after RPV failure

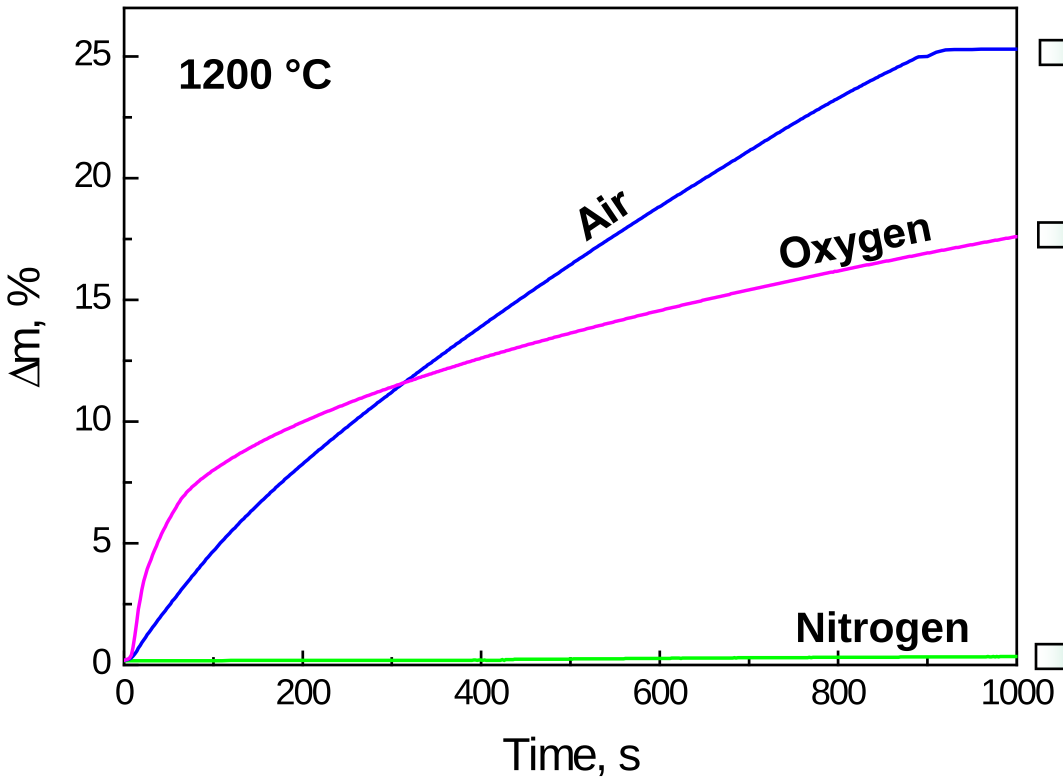


Mid loop operation



Spent fuel storage pool accident

Oxidation of Zr alloys in N_2, O_2 and air



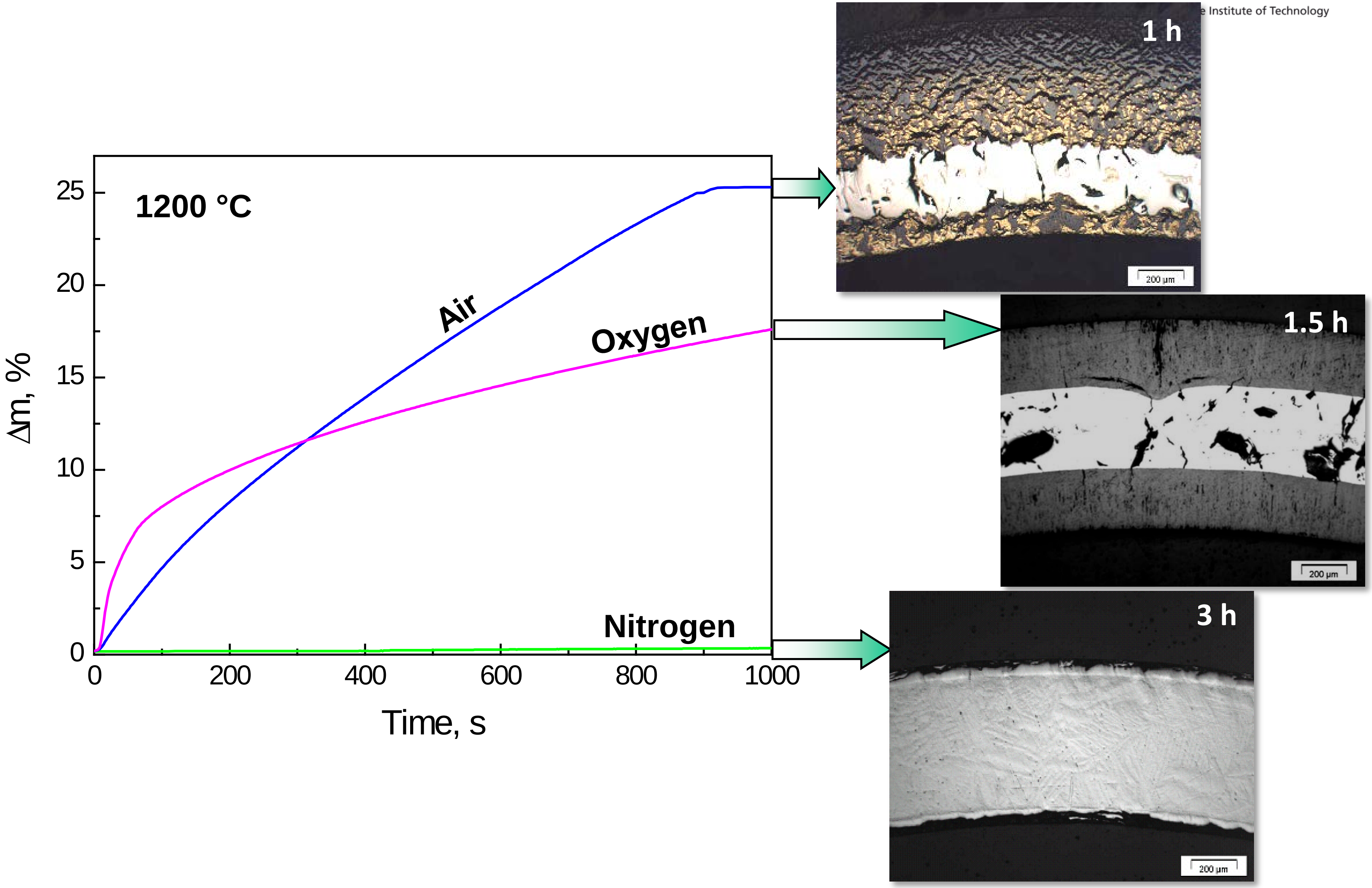
~ Linear oxidation kinetics

Parabolic oxidation kinetics

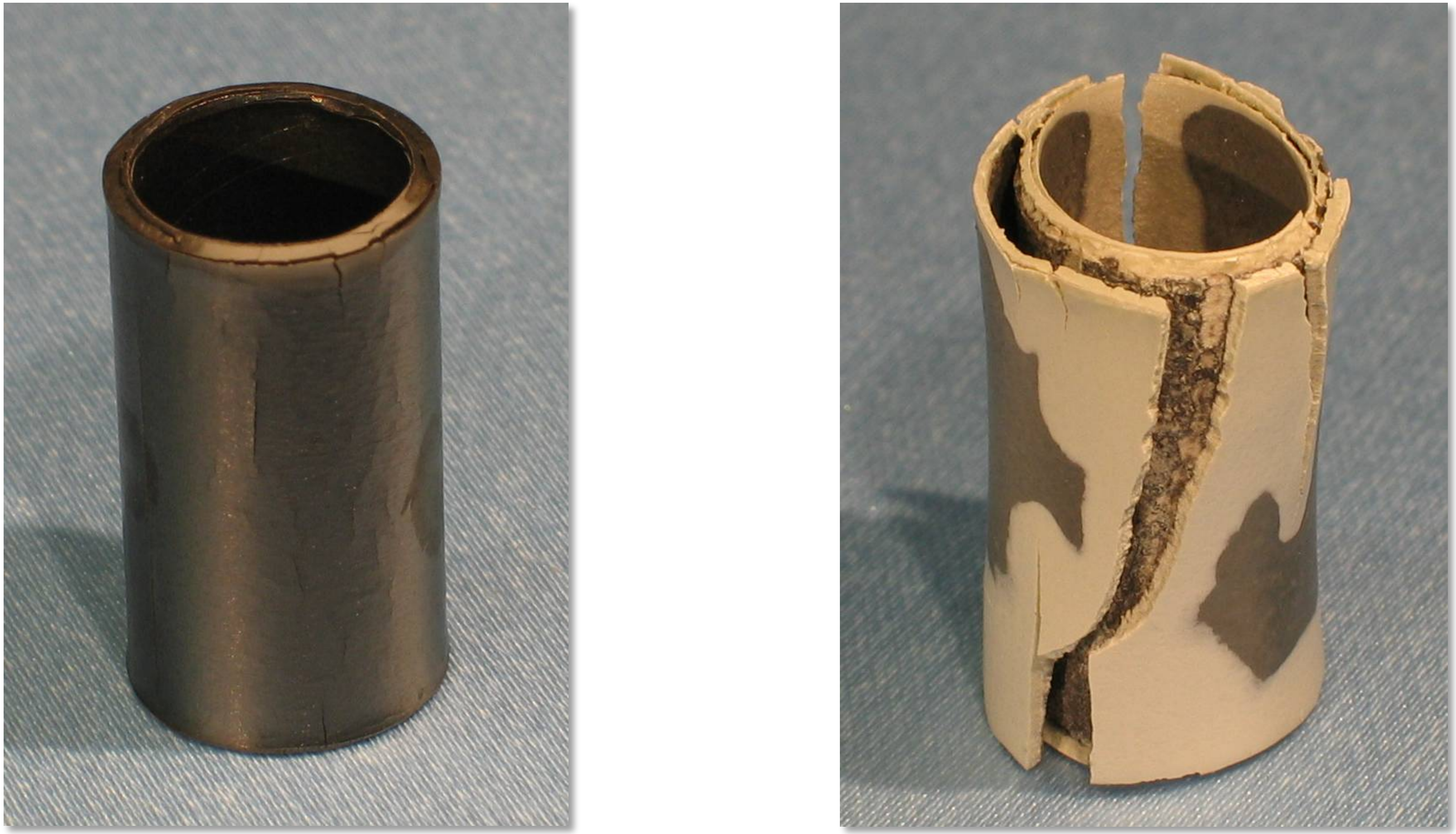
Parabolic reaction kinetics

Oxidation rate in air is much higher than in oxygen or steam

Oxidation of Zr alloys in N_2, O_2 and air



Consequences of air ingress for cladding



1 hour at 1200°C in steam

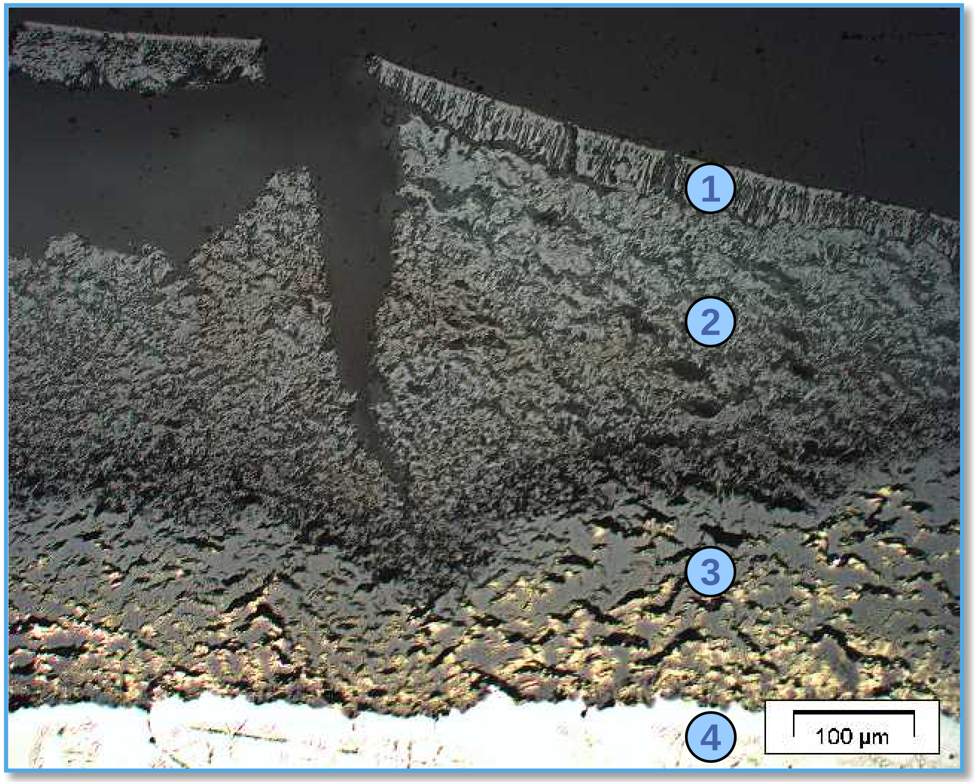
1 hour at 1200°C in air

→ Loss of barrier effect of cladding

Mechanism of air oxidation

- Diffusion of air through imperfections in the oxide scale to the metal/oxide interface
- Consumption of oxygen
- Remaining nitrogen reacts with zirconium and forms ZrN
- ZrN is re-oxidized by fresh air with proceeding reaction associated with a volume increase by 48%

➡ Formation of porous and non-protective oxide scales



1 – initially formed dense oxide ZrO_2

2 – porous oxide after oxidation of ZrN

3 – ZrO_2 / ZrN mixture

4 – α-Zr(O)

Oxidation in mixed steam-air atmospheres

Zry-4, 1 hour at 1200°C

H_2O

0.7 H_2O
0.3 air

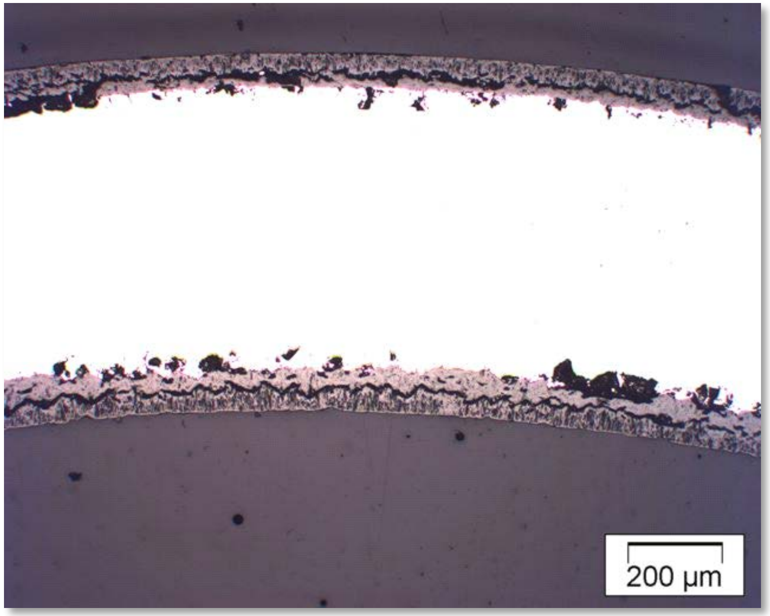
0.3 H_2O
0.7 air

0.1 H_2O
0.9 air

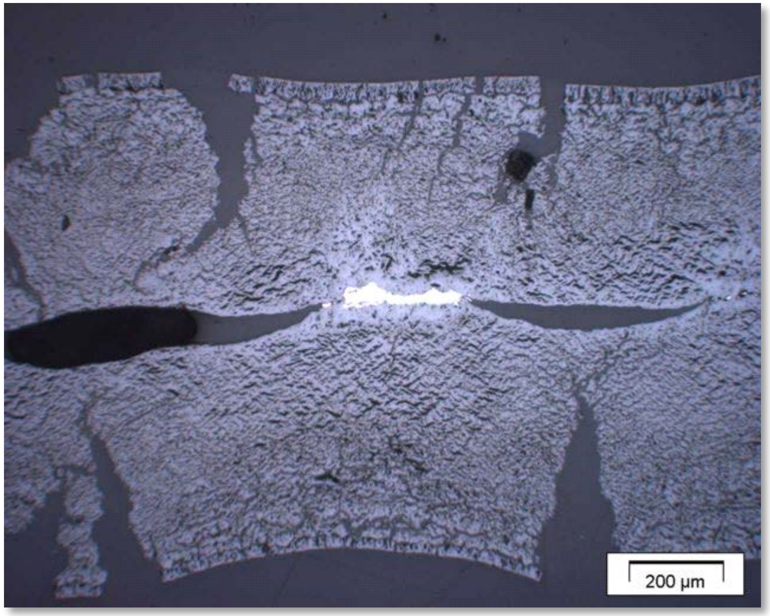
- Increasing degradation with raising content of air in the mixture

Oxidation in mixed atmospheres

1 hour at 1000 °C in steam

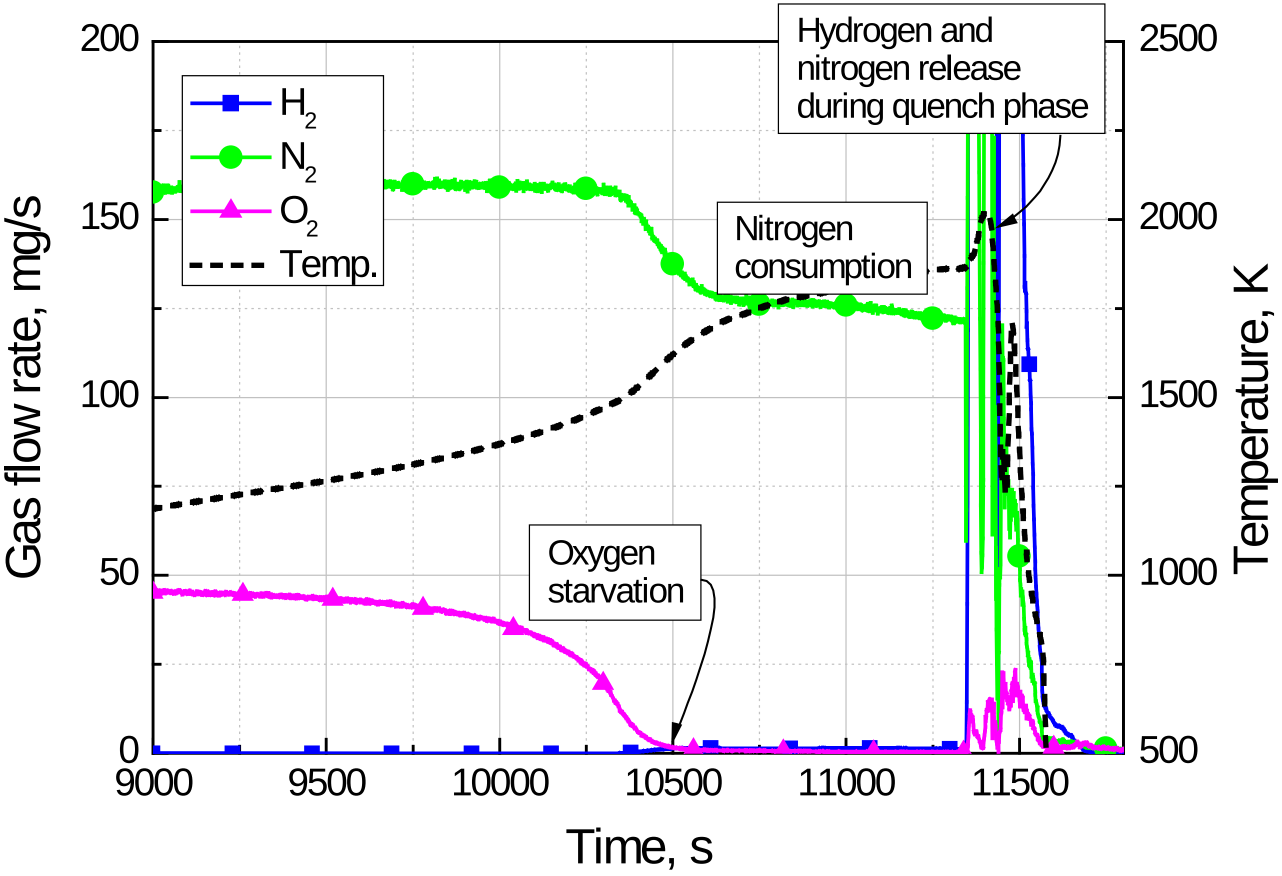


1 hour at 1000 °C in 50/50 steam/N_2

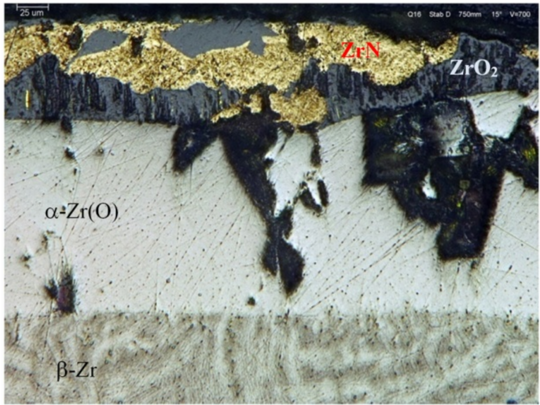


- Strong effect of nitrogen on oxidation and degradation
- Nitrogen acts like a catalyst (NOT like an inert gas)
- Enhanced hydrogen source term by oxidation in mixtures containing nitrogen

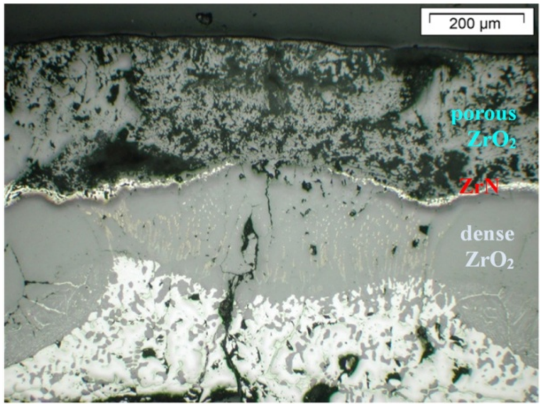
QUENCH-16 bundle test with air ingress



Off-gas composition during the air ingress phase (after pre-oxidation in steam)



ZrN formation at the end of air ingress phase

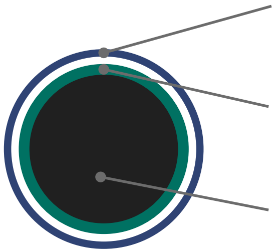


ZrN re-oxidation during quench phase

Absorber materials in LWRs

Boron carbide

- Used in boiling water reactors (BWR), VVERs, some pressurized water reactors (PWR)
- Control rods (PWR) or cross-shaped blades (BWR)
- Surrounded by stainless steel (cladding, blades) and Zry (guide tubes, canisters)



Zry guide tube
T_{melt}=1900°C

SS cladding
T_{melt}=1450°C

B_4C
T_{melt}=2450°C

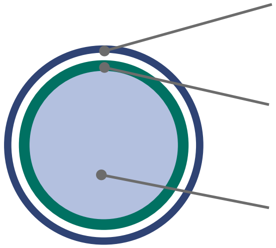
BWR control rod

BWR control blade

AgInCd alloy

- Used in PWRs
- Surrounded by stainless steel cladding and Zry guide tubes
- Rods in Zry guide tubes combined in control rod assemblies

PWR control rod assembly



Zry guide tube
T_{melt}=1900°C

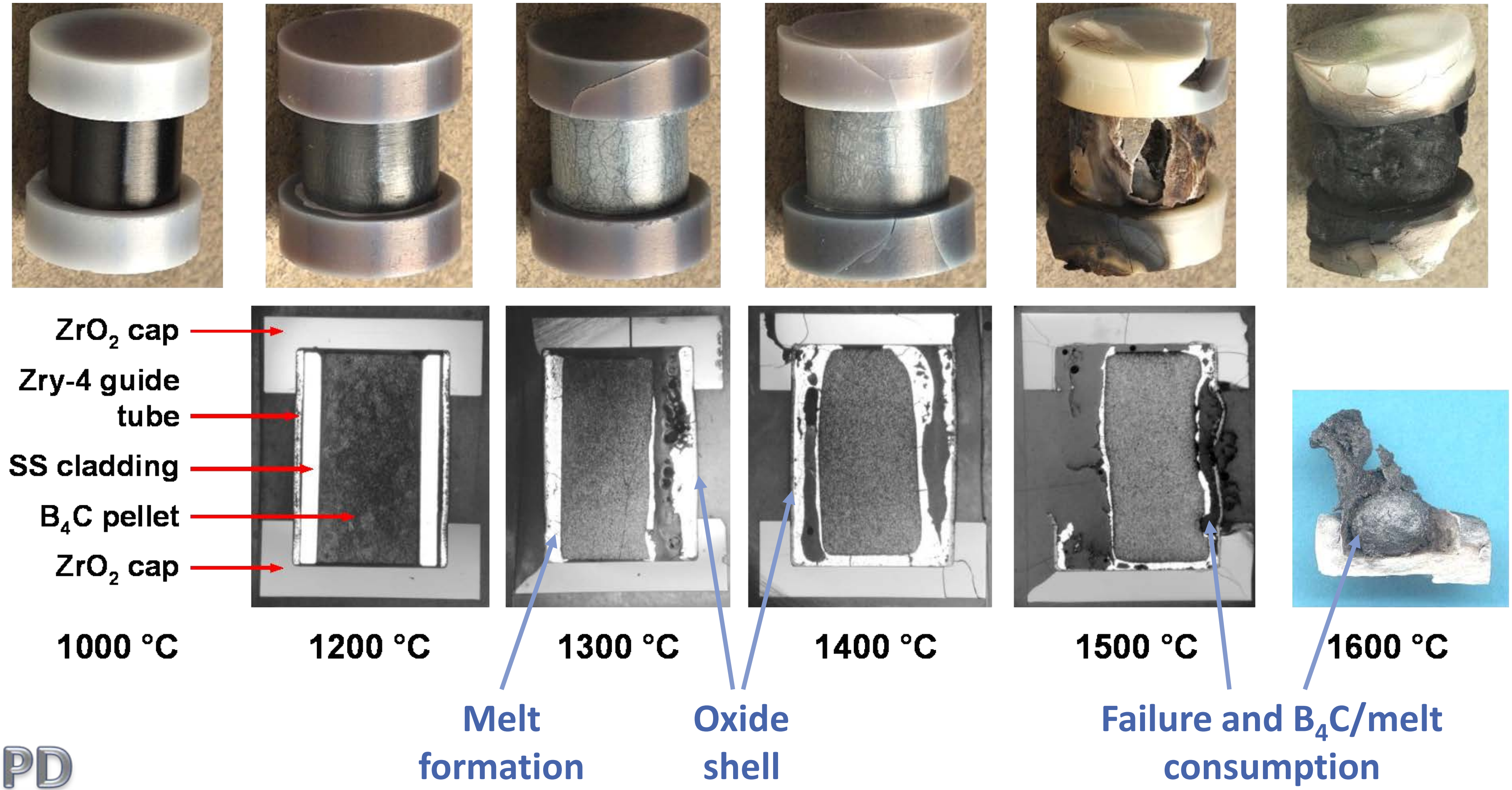
SS cladding
T_{melt}=1450°C

AgInCd
T_{melt}=800°C

PWR control rod

Degradation of B_4C control rods (1-pellet)

Post-test appearance and axial cross section of B_4C/SS/Zry specimens after 1 hour isothermal tests at temperatures between 1000 and 1600 °C

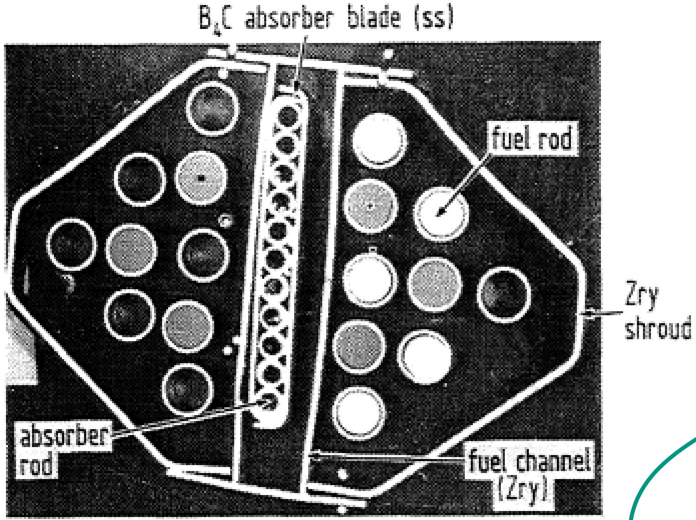


Melt formation

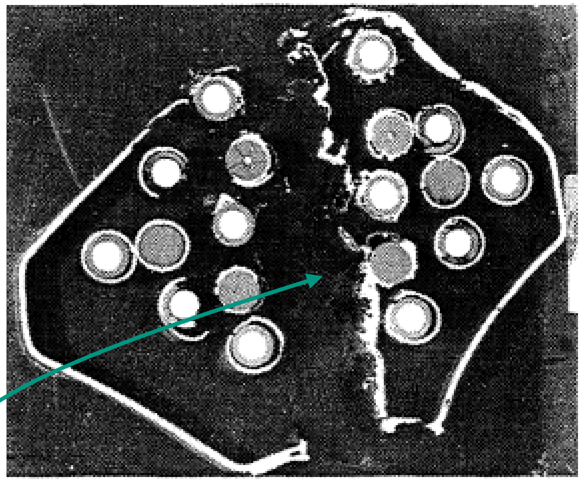
Oxide shell

Failure and B_4C/melt consumption

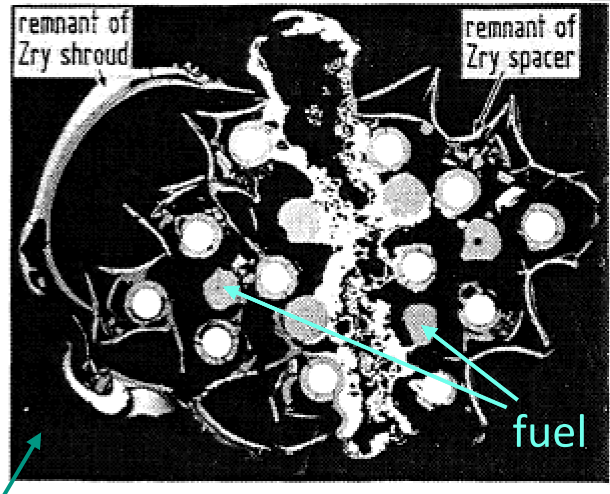
Degradation of B_4C control blade (BWR bundle test) CORA-16



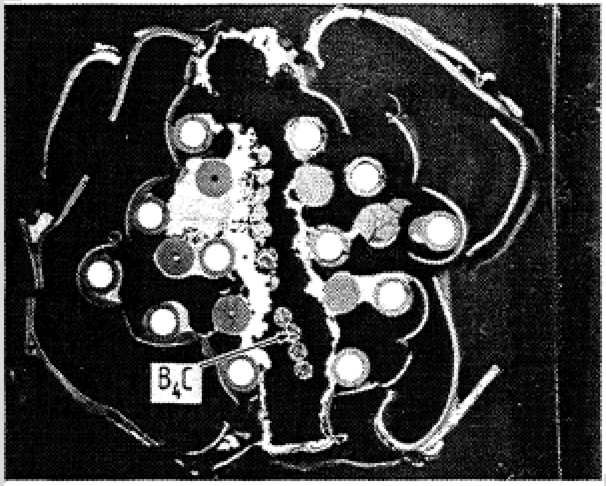
16-08 (1145mm), bottom view



-07 (963mm), top view

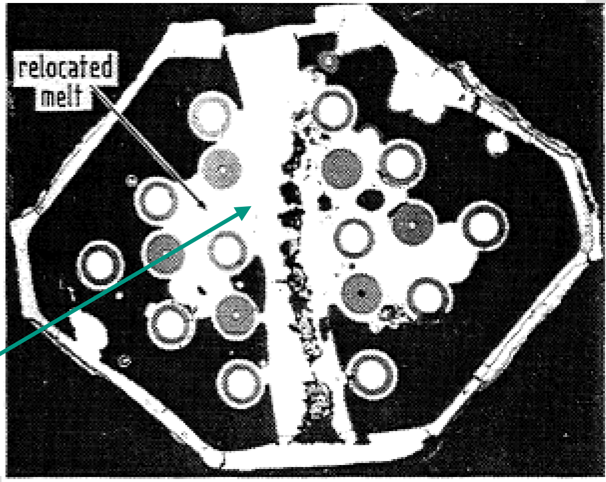


16-09 (525mm), top view
center grid spacer elevation



16-03 (310mm), top view

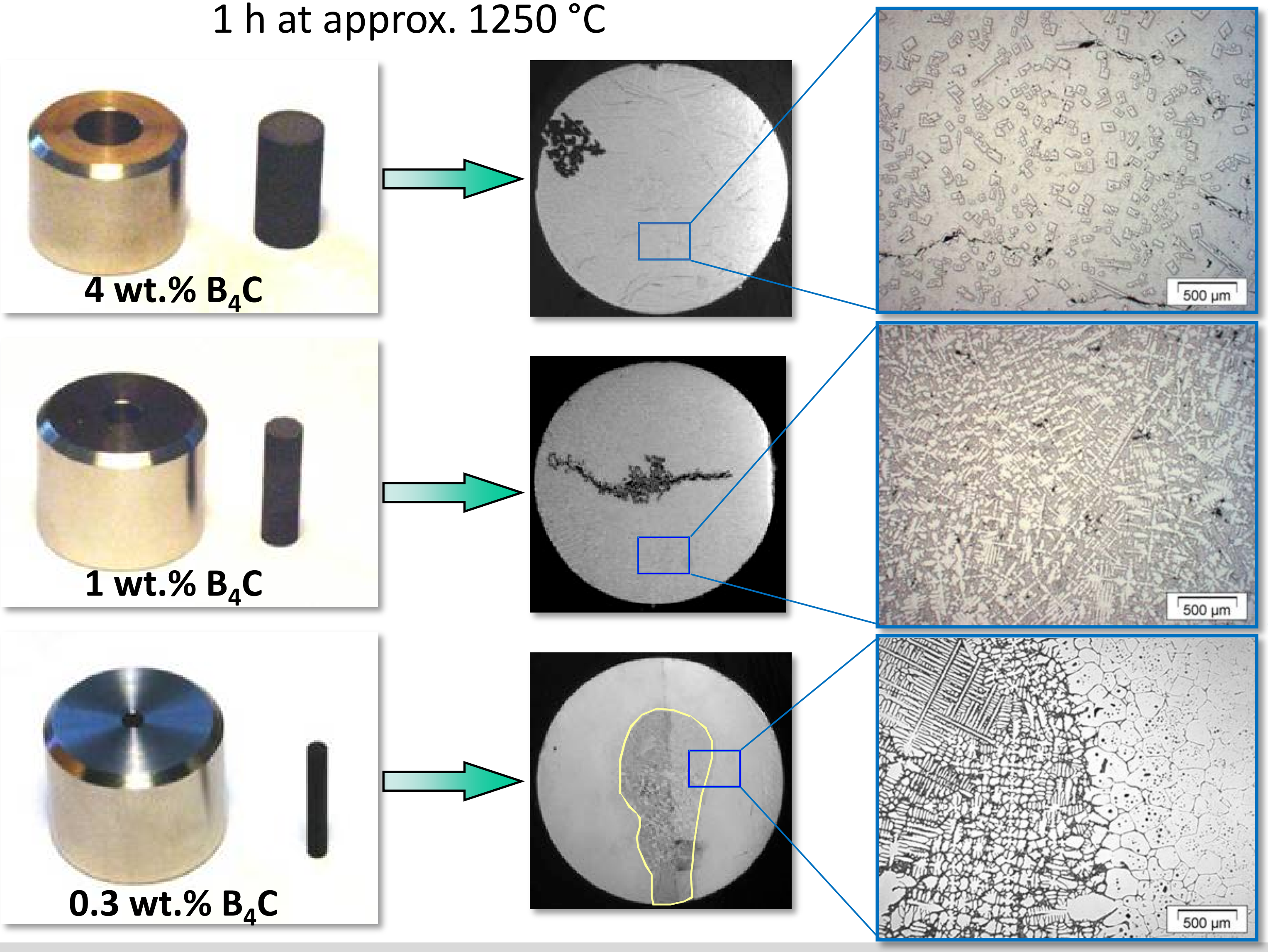
- Complete loss of absorber blade
- Dissolution of cladding and fuel
- Massive melt relocation (B_4C, SS, Zry, UO_2)



16-01 (110mm), top view

Eutectic interaction of stainless steel with B_4C

1 h at approx. 1250 °C



4 wt.% B_4C

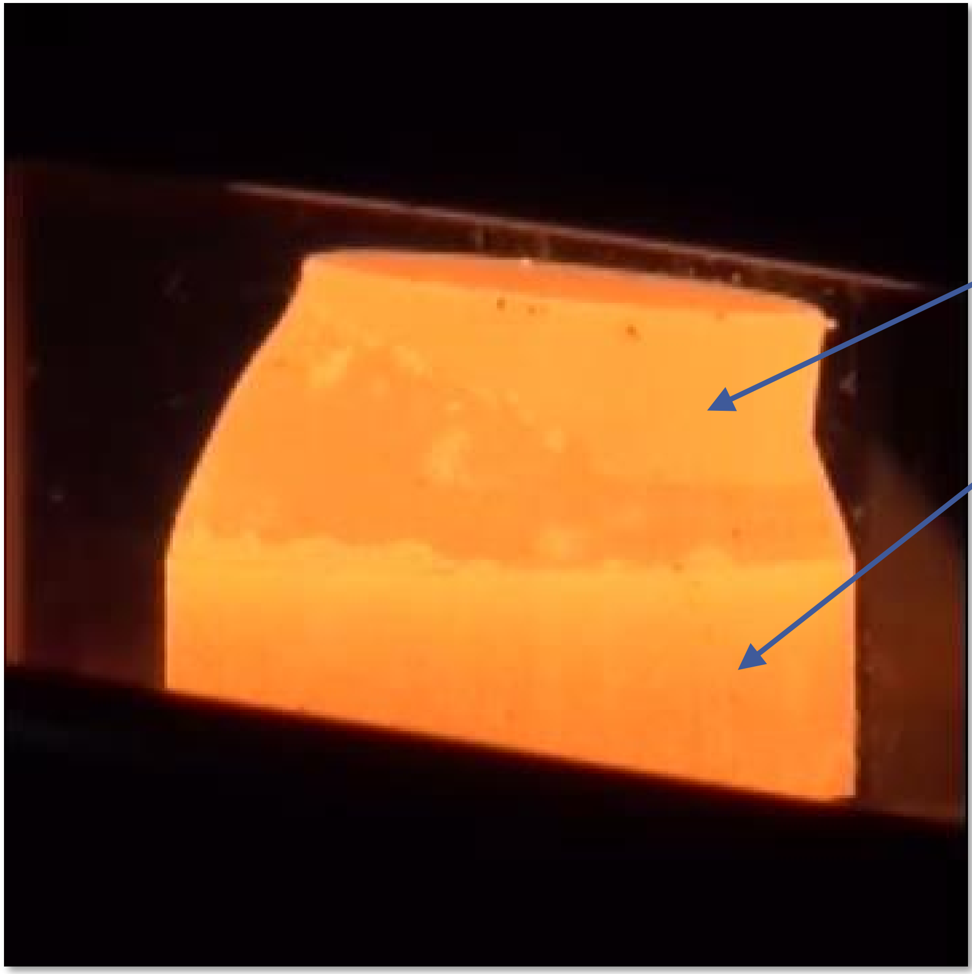
1 wt.% B_4C

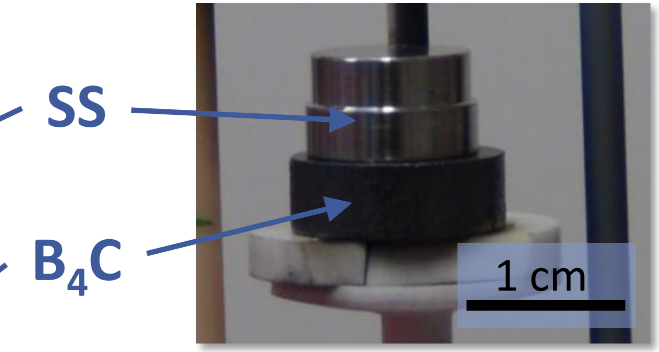
0.3 wt.% B_4C

Complete liquefaction of stainless steel

1/3 of SS liquefied

Eutectic interaction of stainless steel with B_4C





- Rapid and complete melting of SS at 1250°C starting at B_4C/SS boundary

Oxidation of boron carbide; main chemical reactions

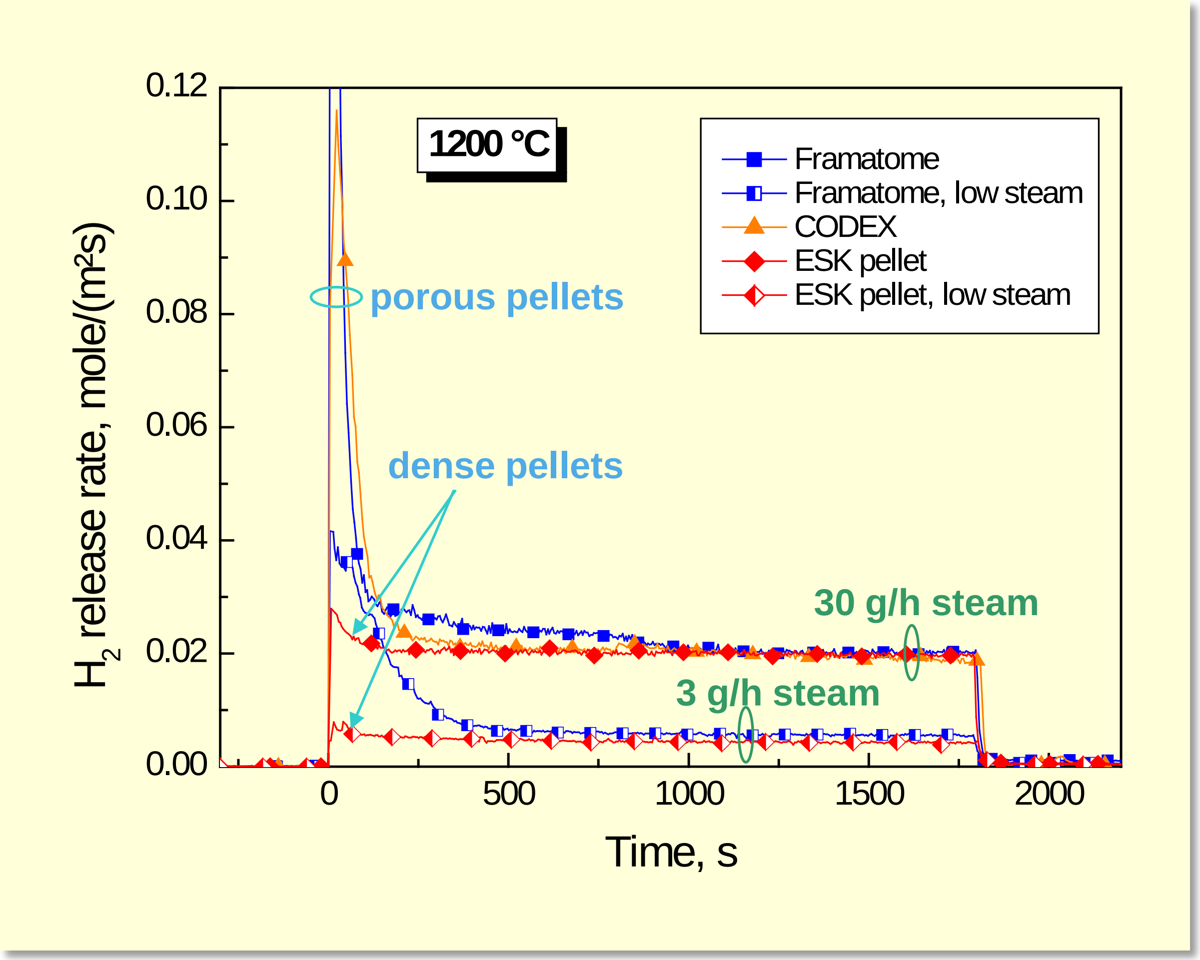
$B_4C + 8H_2O(g) \rightarrow 2B_2O_3(l) + CO_2(g) + 8H_2(g)$ -760 kJ/mol

$B_4C + 6H_2O(g) \rightarrow 2B_2O_3(l) + CH_4(g) + 4H_2(g)$ -987 kJ/mol

$B_2O_3 + H_2O(g) \rightarrow 2HBO_2(g)$ +341 kJ/mol

- Release of hydrogen, various carbon-containing gases and heat
- Formation of a superficial boron oxide layer and its vaporization

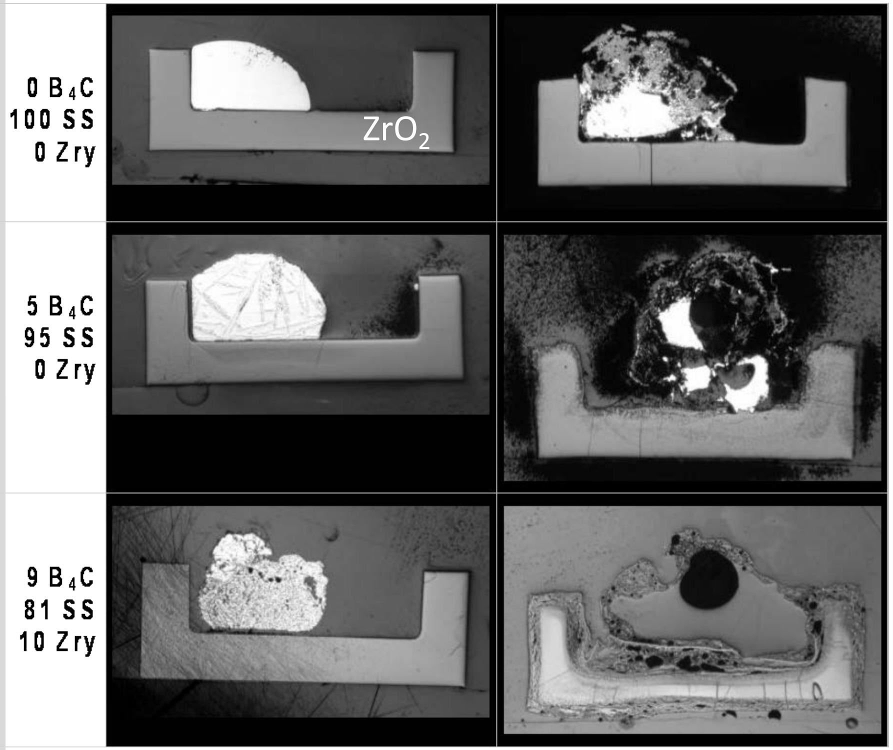
Oxidation kinetics of B_4C in steam



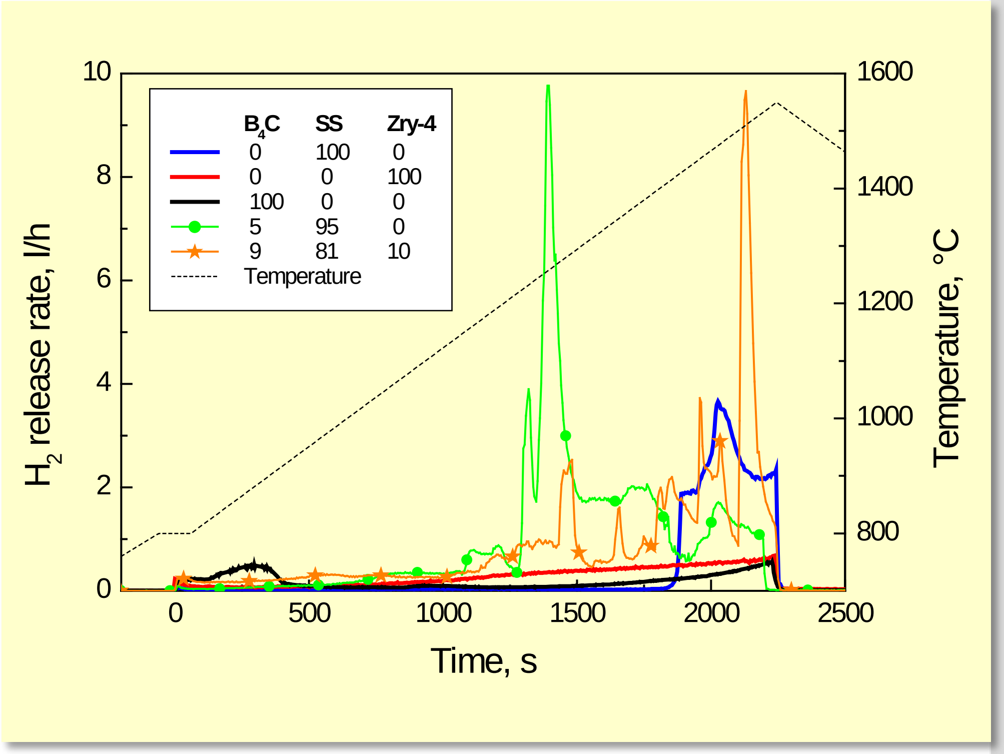
- Strongly dependant on B_4C structure and thermo hydraulic boundary conditions like pressure and flow rate

Oxidation of B_4C absorber melts

Transient oxidation of B_4C/SS/Zry-4 absorber melts
in steam between 800 and 1550 °C



before oxidation after oxidation



Oxidation rate during reaction of absorber melts and pure CR components in steam

Gas release due to oxidation of B_4C (melts)

- Hydrogen
  - Up to 290 g H_2 per kg B_4C
  - Up to 500 kg additional H_2 production for BWRs
- Carbon monoxide/dioxide
  - Ratio depending on temperature and oxygen activity
  - Non-condensable gases affecting THs a
  - CO combustible and poisonous
- Methane
  - Would have strong effect on fission pr
  - Bundle experiments and SETs reveal o
- Boric acids
  - Volatile and soluble in water
  - Deposition at colder locations in the circuit

Energetic effects of B_4C oxidation

- Oxidation of B_4C in steam: 13 MJ/kg_{B4C}
- Oxidation of B_4C in oxygen: 50 MJ/kg_{B4C}

➡ Significant contribution to energy release in the core

For comparison:

- Oxidation Zr in steam: 6 MJ/kg_{Zr}
- Fuel value of mineral oil: 12 MJ/kg_{oil}
- Fuel value of black coal: 30 MJ/kg_{coal}

Possible consequences for Fukushima accidents

- Boiling water reactors with cruciform-shaped blades
- 1 control blade = 7 kg B_4C + 93 kg SS
- ➡ Complete liquefaction of the blade at T>1200°C

Fukushima Daiichi NPPs:

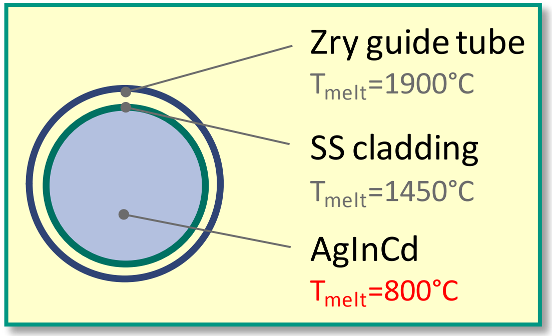
- Unit 1: 97 control blades
- Unit 2-4: 137 control blades

- Complete oxidation of B_4C inventory by steam:
- ➡ 195/275 kg H_2
- ➡ 2700/3800 kWh (10/14 GJ)

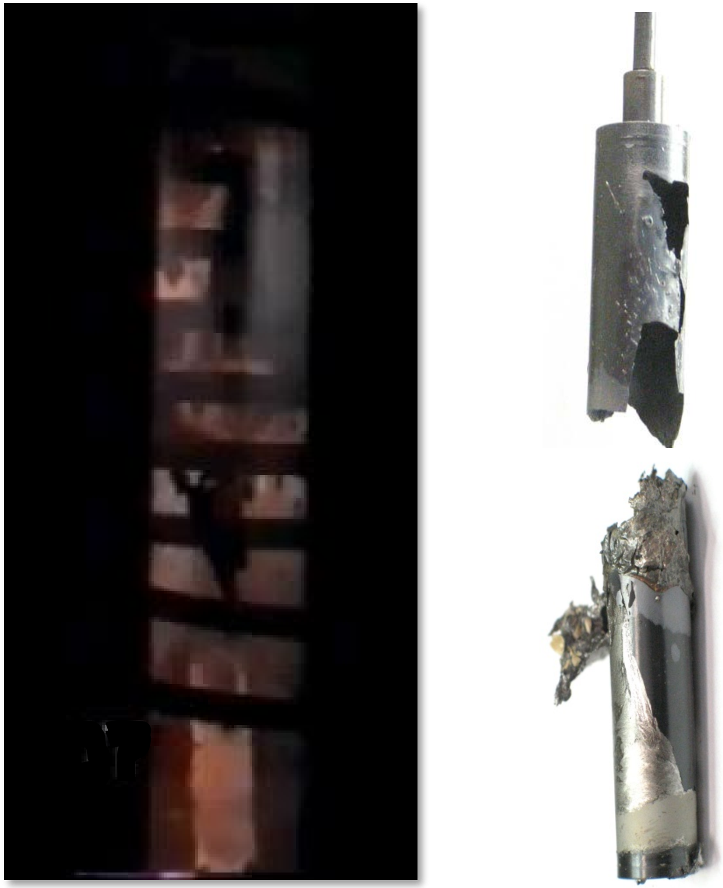
BWR control rod

Failure of AgInCd absorber rod

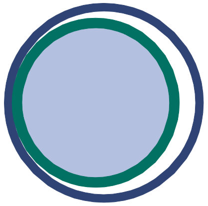
- Ag-In-Cd control rods fail at temperatures above 1200°C due to the eutectic interaction between SS and Zry-4
- Failure is very stochastic (from local to explosive) with the tendency to higher temperatures for symmetric samples and specimens with inner oxidation
- No ballooning of the SS cladding tube was observed before rupture
- Burst release of cadmium vapour is followed by continuous release of indium and silver aerosols and absorber melt



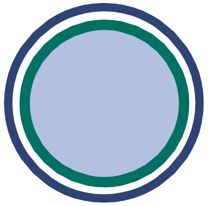
Different failure types of AgInCd absorber rod



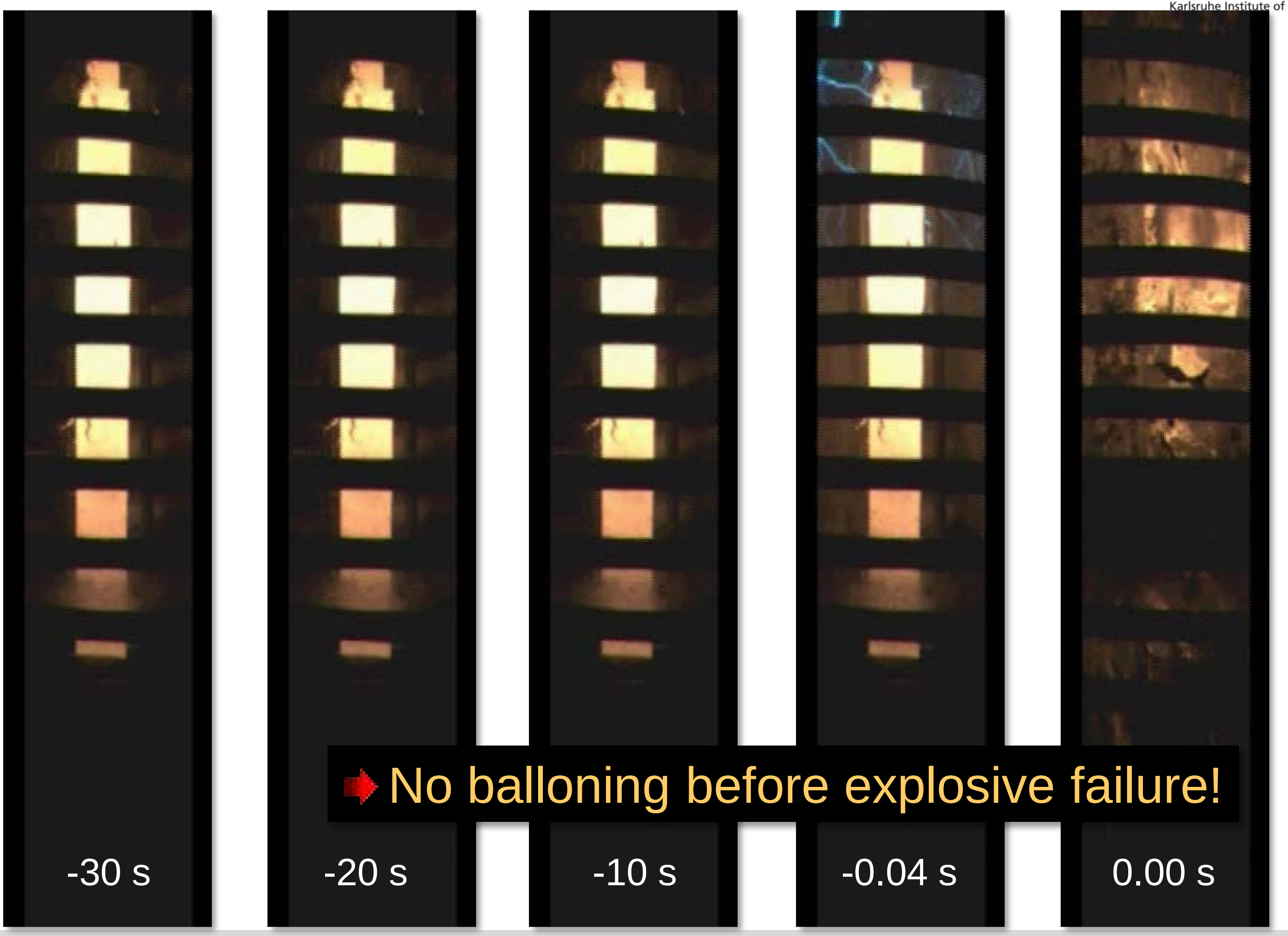
SIC-02 (asym. rod)
Local failure at 1230°C



SIC-05 (symmetric rod)
Global failure at 1350°C

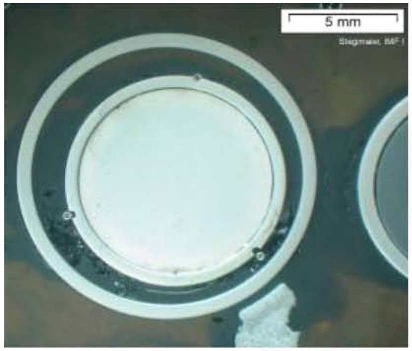


Explosive failure of SIC-11 w/o Zry guide tube

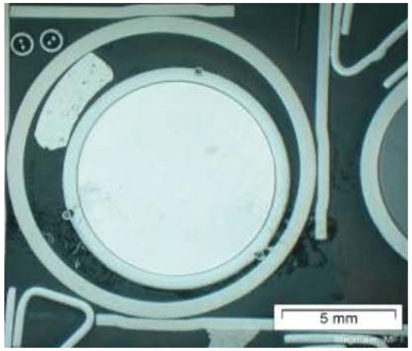


No balloning before explosive failure!

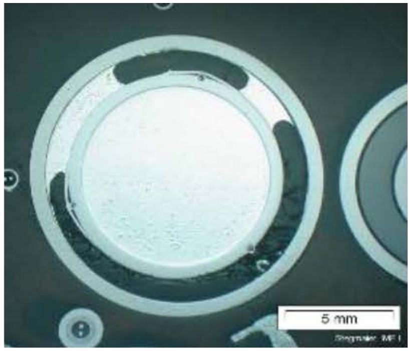
QUENCH-13 control rod appearance



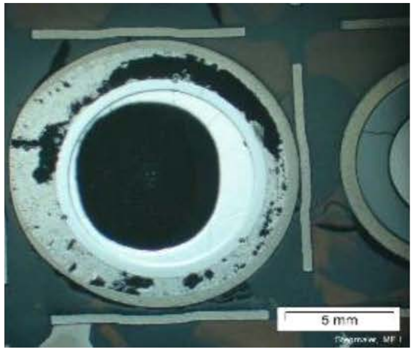
50 mm 540°C



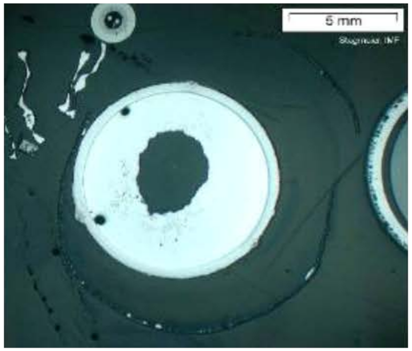
170 mm 650°C



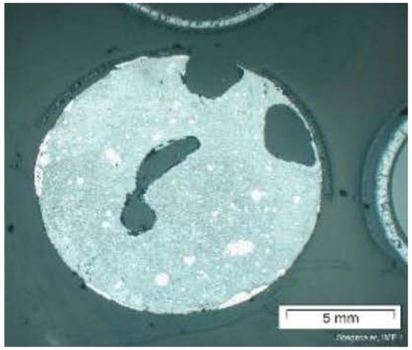
350 mm 850°C



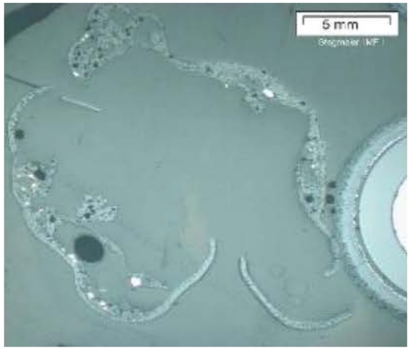
550 mm 1026°C



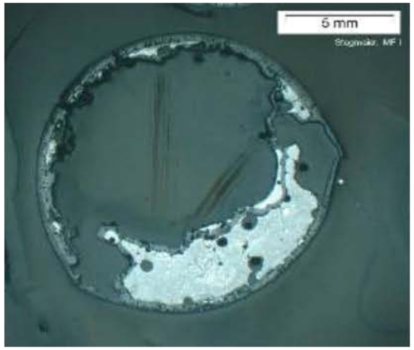
750 mm 1280°C



850 mm 1437°C



950 mm 1418°C

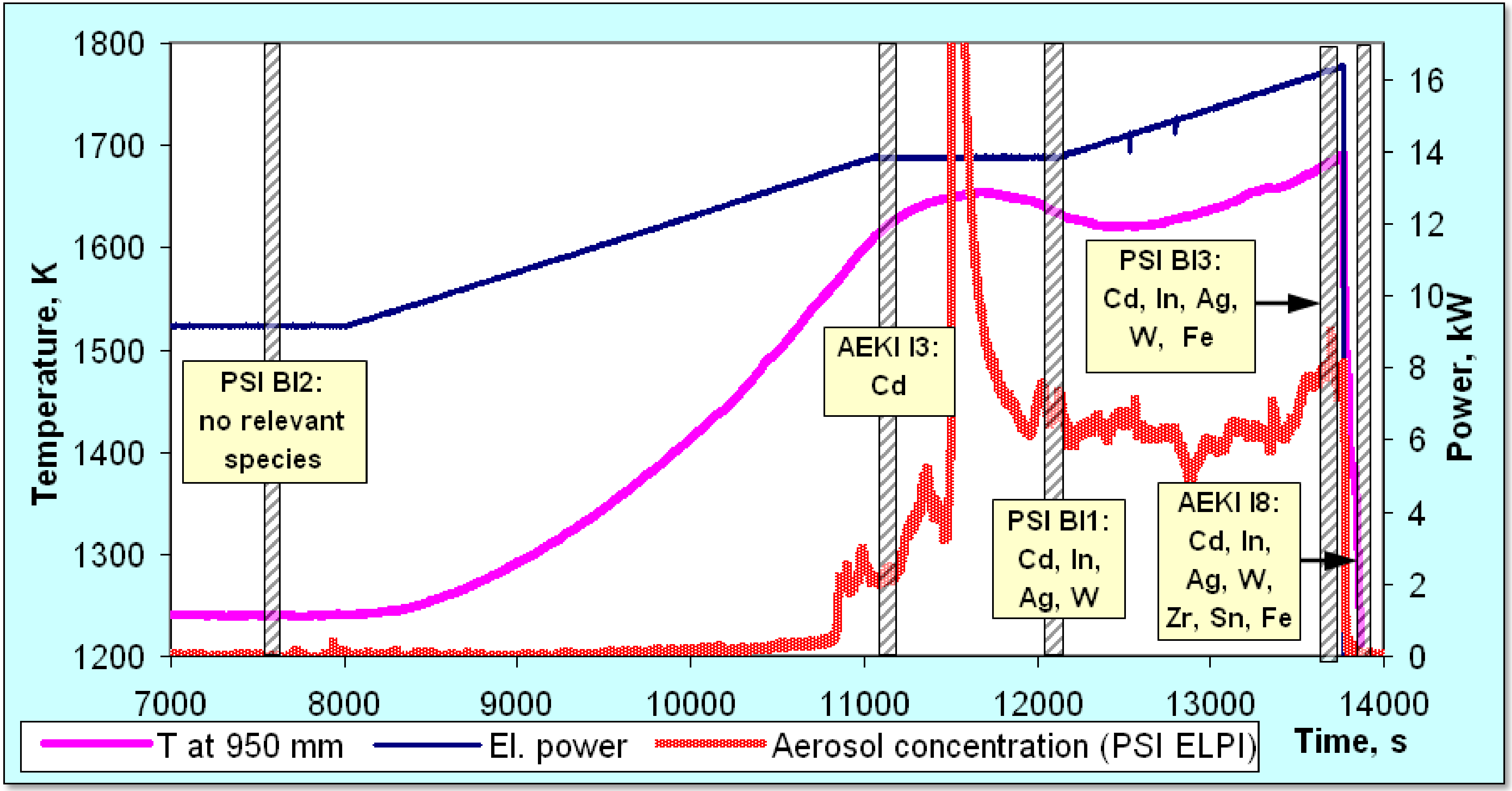


1050 mm 1216°C

- No direct interaction between AIC and steel
- Increasing interactions between relocated AIC and Zry in gap with temp.
- Increasing interaction between melt and steel with increasing Zr content

QUENCH-13 bundle test: aerosol release

- First burst release of cadmium vapor, then aerosols mainly consisting of silver and indium



Summary

- Chemical interactions may strongly affect the early phase of a severe nuclear accident.
- The main hydrogen source term is produced by metal-steam reactions
- Exothermal chemical reactions can cause heat release larger than the decay heat and hence strongly contribute to the power generation in the core
- Nitrogen does not behave like an inert gas during the conditions of a severe accident
- Eutectic interactions between the various materials in the core (i.e. B_4C-SS, SS-Zry) cause liquefaction of materials significantly below their melting temperatures
- Boron carbide may (at least locally) significantly contribute to release of heat, hydrogen and other gases

Karlsruhe Institute of Technology

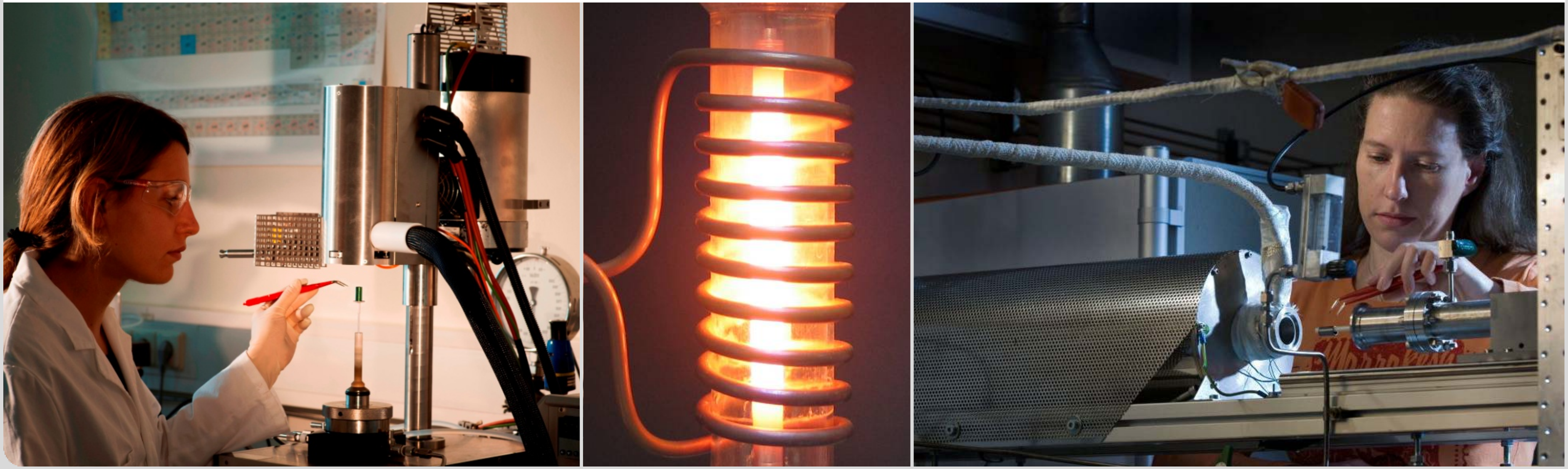
Institute for Applied Materials

High-temperature oxidation and mutual interactions of materials during severe nuclear accidents

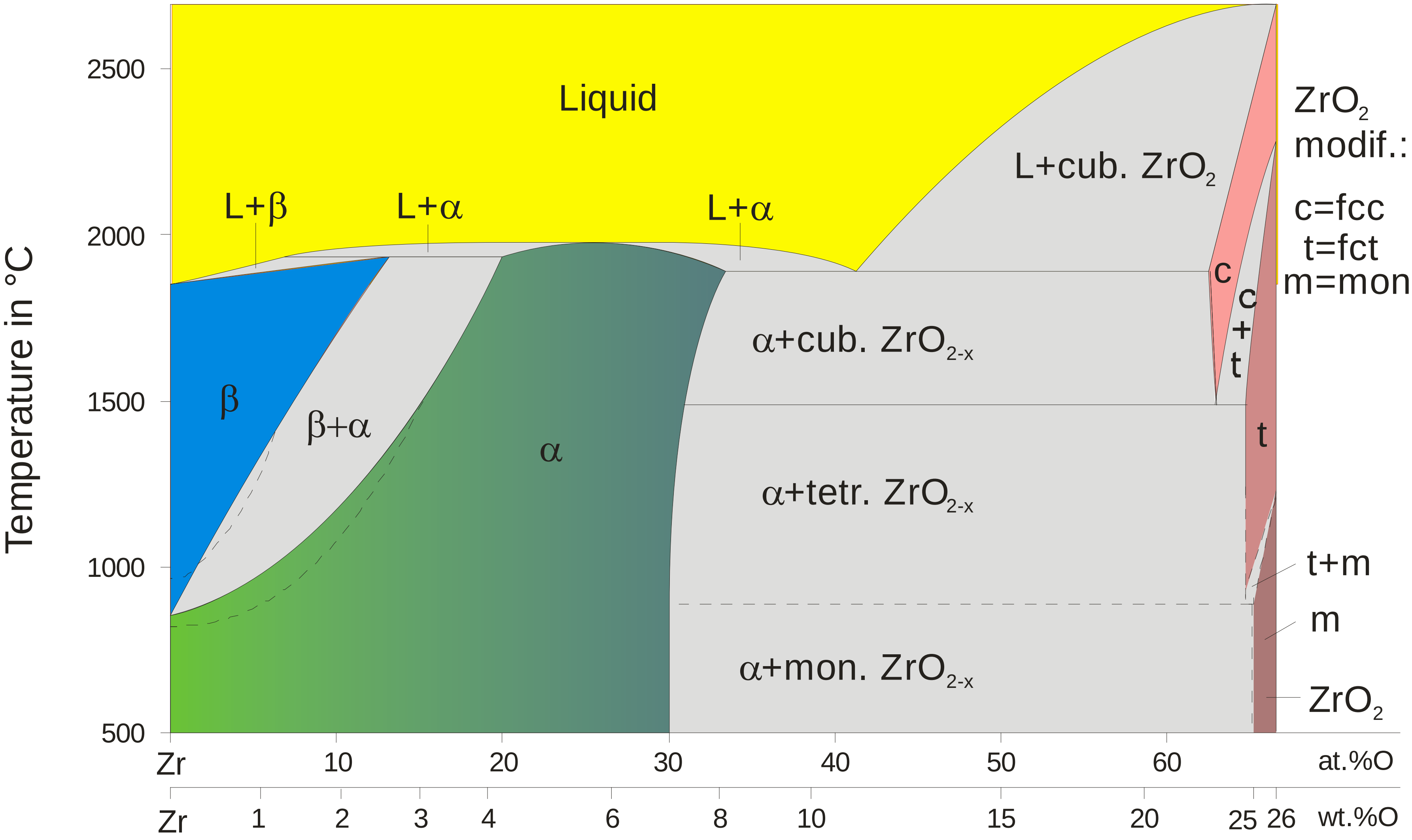
Martin Steinbrück, **Mirco Große**, **Juri Stuckert**

NuMat2012, 21-25 October, Osaka, Japan

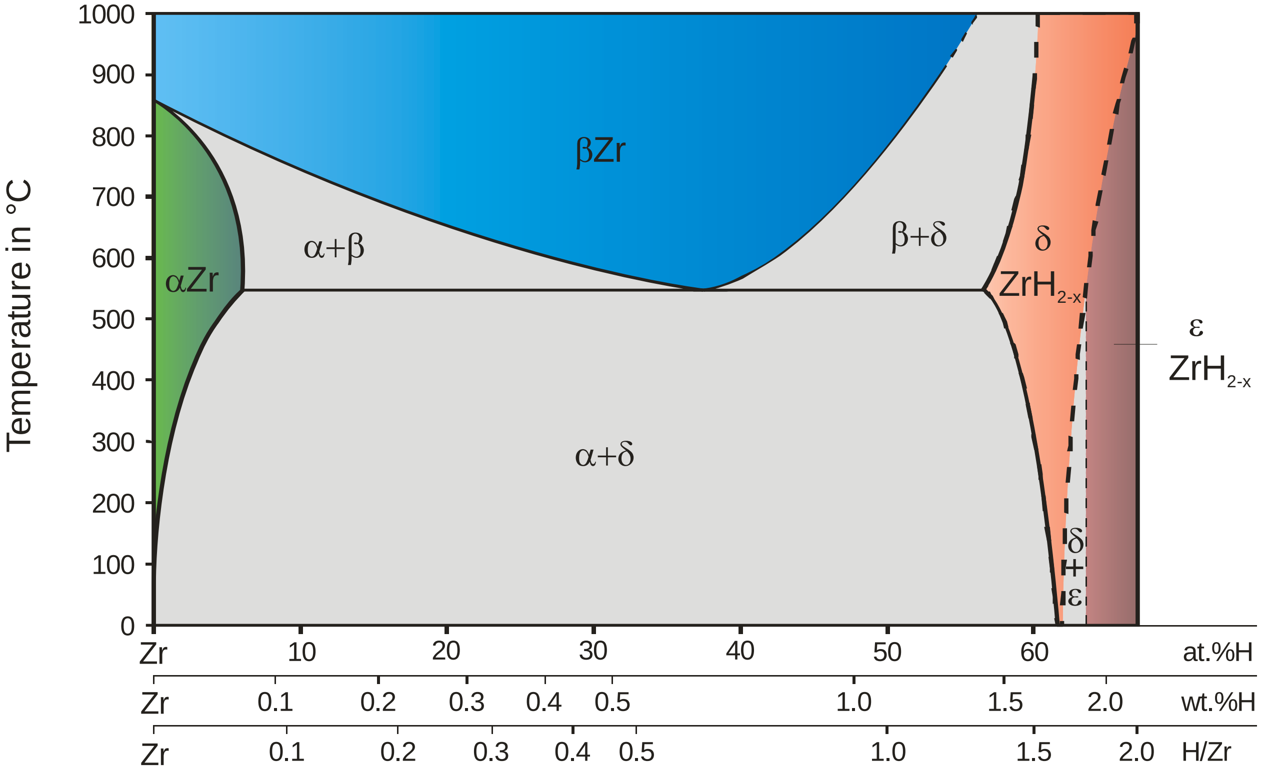
Institute for Applied Materials IAM-AWP & Program NUKLEAR



Phase diagram Zr - O



Phase diagram Zr - H



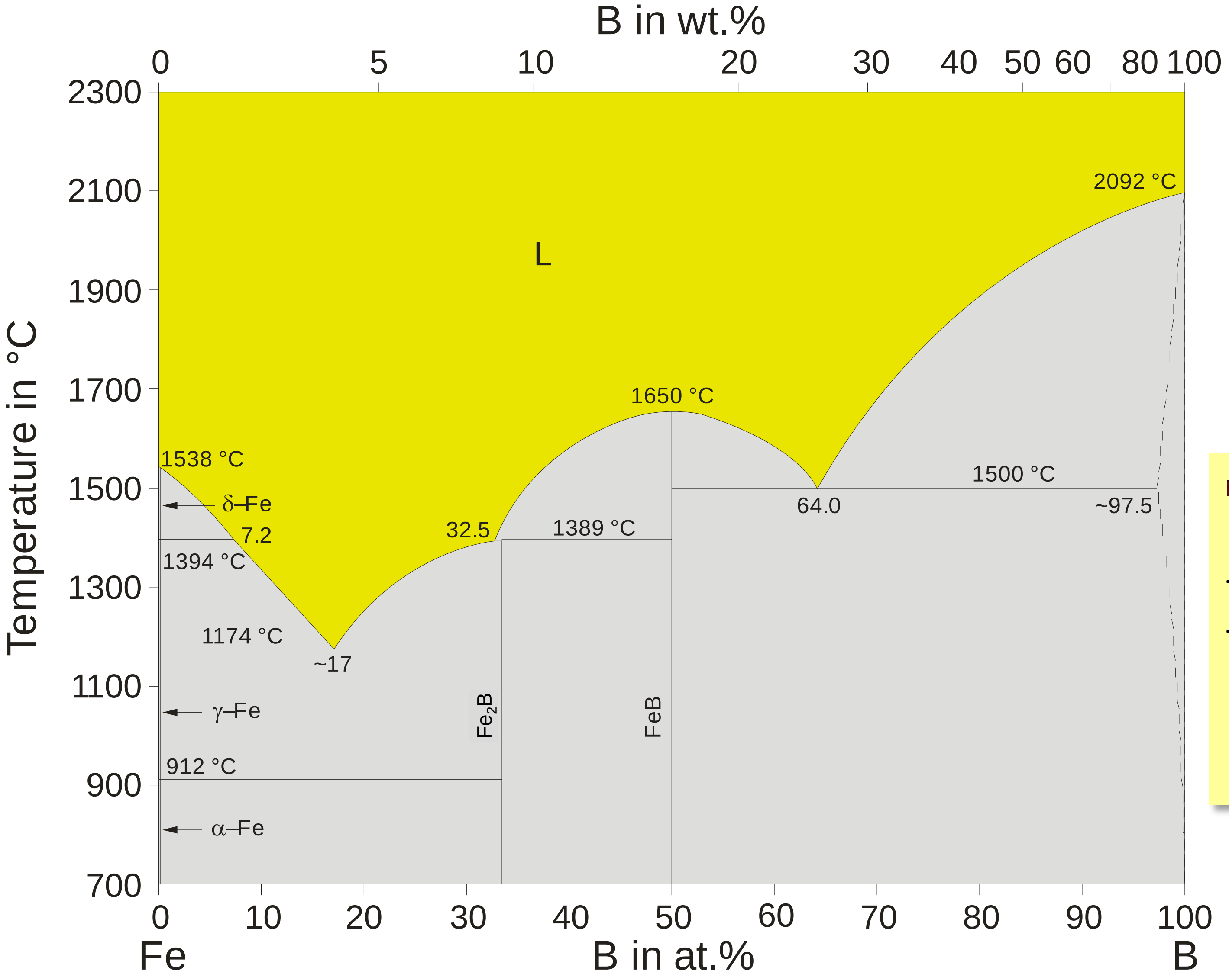
Sieverts' law:

$$\frac{H}{Zr} = k_S \cdot \sqrt{p_{H_2}}$$

with

$$k_S = A \cdot e^{\frac{-B}{RT}}$$

Phase diagram iron - boron



Decrease of melting temperatures due to eutectic interactions